

Observations, &c. (*continued*).

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BAKERIAN LECTURE.—“The Discharge of Electricity through
Gases. (Preliminary Communication.)” By ARTHUR
SCHUSTER, F.R.S. Received and Read March 20, 1890.

“If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity.”
—HELMHOLTZ (Faraday Lecture).

I. *Introduction.*

The phenomena of the electric discharge in gases excite a wide-spread interest at the present time. It could hardly be otherwise; for although our knowledge of electric manifestations is increasing in all directions, we cannot be assured of the correctness of our explanations while the mysterious appearance of the gas discharge remains unexplained. As long as we still have to account for a series of most puzzling facts, it seems possible that we are on the wrong road altogether, and that there may be some surprise in store for us which will ultimately compel us to reconsider all our present ideas. I have endeavoured during the last ten years to study the gas discharge, with a view to finding some explanation which should be in agreement with the conclusions drawn from other parts of physics.

In the year 1884 I presented to the Royal Society* an outline of a

* ‘Roy. Soc. Proc.,’ vol. 37, p. 317 (1884).

theory which seemed to me to form a hopeful starting point for future investigation. I have every reason to be satisfied with the way in which that theory has been received by other workers in the same field, and I think that, in spite of difficulties, which I do not wish to underrate, it is generally considered to have a good chance of ultimate success. I have since been able to extend my views, and am bold enough to think that we may now form a fairly complete idea of the most important features of the gas discharge.

In 1882, that is, two years before my paper was presented to the Royal Society, Mr. Giese* was led, by a study of the electric conductivity of the gases which rise from flames, to the identical hypothesis which formed the basis of my paper. I much regret that I have only recently become acquainted with Mr. Giese's work, as I should have been glad to have drawn attention to it.

We both assume that each molecule of a gas contains atoms which carry equal and opposite charges; and that these charges are the same as those carried by the ions in electrolytes; that, further, a current of electricity through a gas can only be maintained by a diffusion of the charged atoms through it. I have never claimed much originality for this hypothesis, as the same idea must have occurred to many others, and it would probably be difficult to trace its early history. The hypothesis of definite charges only forms a small part, however, of the theory which I have sketched out in my previous paper. By itself alone it is not sufficient to account for the observed facts. In order to distinguish the theory from others, I shall call it the theory of "electrolytic convection," as it resembles in many ways the kind of conduction in liquids which has been described under that name by Helmholtz. The theory of electrolytic convection offers obvious explanations of a number of different phenomena, as has been shown by Giese for the discharge through gases rising from flames, by myself for the discharge introduced by strong electromotive forces, and by Elster and Geitel for a number of other phenomena. According to this theory, a gas insulates as long as there are no free ions present, but acts as a conductor as soon as, through some cause or other, the molecules are split up into ions. We meet with formidable difficulties, however, when we come to discuss the transference of electricity between the solid conductor and the gas; for here we are to a great extent tied down by our knowledge of electrolysis in liquids. We know that a difference of potential of 2 volts between the electrodes is sufficient to decompose water, and therefore to allow the interchange of electricity between the metal and the ion of hydrogen or oxygen. No theory of gas discharges is admissible which cannot be brought into harmony with these facts.

* 'Wiedemann, *Annalen*,' vol. 17, p. 537 (1882).

Definition of Unipolar Conductivity.

An electrode often discharges electricity of one kind more freely than that of the opposite kind. The phenomenon has been called that of unipolar conductivity, but we evidently require some understanding as to when we shall call a gas or an electrode positively unipolar. If a positive charge on an electrode becomes more quickly dissipated than a negative charge, we may either say that the electrode discharges positive electricity more rapidly into the gas, or that the gas discharges negative electricity more rapidly into the electrode. Some confusion may be caused by the fact that different writers have looked at the question from different sides and have not adopted a uniform nomenclature. I shall call an electrode positively unipolar if it discharges positive electricity more freely into the gas than negative electricity.* A great part of the following paper will deal with the circumstances under which the exchange of an ion between the conductor and the molecules or atoms takes place, and it will be shown how the peculiar behaviour of gases may be explained. This I consider an important step in support of the theory.

Such expressions as "surface resistance" or "counter electromotive force" have often been employed in cases where they seem to me to be quite unsuitable, and I shall therefore avoid them altogether; but I may occasionally briefly speak of an impediment to the passage of electricity at an electrode, meaning that a rapid fall of potential at that electrode is required to introduce or maintain the discharge.

Circumstances under which the Discharge takes place.

It will be convenient to divide the subject into two main parts: the one dealing with the circumstances under which a discharge can take place, and the other with the phenomena of the discharge itself. It is well known that, if one of two conductors, separated by a gas, is electrified while the other is connected to earth, the gas acts as a perfect insulator as long as the difference of potential between them does not exceed a certain value; if it does, the dielectric strength of the medium breaks down.

It is a matter of some doubt whether, if a spark passes between two conductors of different form, as for instance between a sphere and a plane or between a point and a sphere, the striking distance is different in the two directions. There probably is some difference of this nature in favour of a more easy escape of positive electricity,

* Elster and Geitel in a recent publication have adopted a different nomenclature. They say that a glowing platinum wire in oxygen discharges negative electricity more easily than positive, meaning that the electrode allows a free passage to negative electricity from the gas to the electrode ('Wiedemann, *Annalen*, vol. 38 (1889), p. 39).

though the want of symmetry is not very marked. The important measurements of Wiedemann and Rühlmann* are generally taken to prove a more easy escape of negative electricity under reduced pressure; but when a number of sparks are taken in rapid succession, as they were in these experiments, recent researches seem to indicate that the gas and electrodes may not return to their original condition between the discharges. The consequence is that such a rapid succession of sparks shows some of the phenomena of the continuous current, and the want of symmetry is therefore of the same nature as that which belongs to the discharge, and has nothing to do with the circumstances which determine whether a discharge shall pass or not. The same remarks apply to Lichtenberg figures and Priestley's rings; they are complicated cases of phenomena which are best studied by means of the continuous current. I pass on to consider the cases where a current may pass between two electrodes, the difference of potential being small.

We have four different ways of converting the gas into a conductor, and our subject must be subdivided accordingly. If the electrodes are either (1) heated to redness or (2) illuminated by ultra-violet light, the discharge passes even when the difference of potential does not amount to more than a few volts. Further (3), it has long been known that flames do not behave as dielectrics; and, finally (4), gases through which a discharge is passing have been shown to conduct freely.

(1.) *Discharge from Glowing Electrodes.*

Edward Becquerel,† as far as I know, was the first to discover that air between red-hot platinum electrodes ceases to insulate, and he points out that when the two electrodes are of different sizes, the equalisation of potential takes place more quickly if the larger electrode is negative. Guthrie,‡ by a different method of experimentation, found that red- or white-hot iron balls discharged electricity more easily when positive than when negative.

Looking at the question from the point of view of the theory of electrolytic convection, it seems of the greatest importance to decide whether the discharge from hot bodies is accompanied by any chemical action or not. Mr. Arthur Stanton has conducted in my laboratory a research intended to throw light on the question. The experiments were planned and independently carried out by him, and his own account of them appears (p. 559) as an Appendix to this paper. But I must briefly allude to his results, which I consider to be of great importance.

* 'Poggendorff's Annalen,' vol. 145, pp. 235, 364 (1872).

† 'Annales de Chimie,' vol. 39, p. 355 (1853).

‡ 'Phil. Mag.,' vol. 46, p. 257 (1873).

Behaviour of Copper Electrodes.—Let us first consider the case of conductors charged negatively. Clean copper, heated to a full redness in air, is found to discharge negative electricity freely, but, if oxidised carefully all over the surface, it will retain its charge. If on the other hand oxidised copper is heated in hydrogen instead of in air, it will be quickly discharged until all the oxide is reduced; after that, the charge will be retained. In other words, negative electricity is quickly discharged during the process of oxidation or deoxidation, but not otherwise, as when clean copper is heated in hydrogen or oxidised copper in air. So far as the experiments could be carried out with iron in place of copper they gave similar results. As regards the behaviour of copper when it is positively electrified, the phenomena are not so sharply defined. Positive copper in an atmosphere of hydrogen seems certainly to discharge itself, even when perfectly reduced, so that it retains a negative charge. Copper in air seems to discharge positive electricity less freely when it is oxidised than during the process of oxidation, but whether it ultimately retains its charge in all cases or not has not yet been completely determined. Preliminary experiments in nitrogen have given the same results as those observed in hydrogen, leakage taking place when red-hot copper is electrified positively, but not when it is electrified negatively.

These experiments tend to show that the process of oxidation or deoxidation can powerfully affect the facility of discharge from red-hot iron or copper; so much so that no very extraordinary precautions are necessary to destroy all signs of leakage of a negative charge. We are not justified as yet in asserting that the discharge of negative electricity is *always* accompanied by a chemical action even with the metals experimented upon, for the temperature at which the experiments were carried on was limited by the danger of melting the copper, and the leakage was only tested by the more or less rapid collapse of two gold leaves connected with the charged body. A higher temperature might have brought out the leakage again, or even at a red heat more delicate methods might have shown that the leakage was only greatly reduced, but not destroyed. As regards positively charged bodies, it is still an open question whether chemical action plays any part in regulating the rate of discharge. The gold leaves collapsed quickly when copper was heated in hydrogen, but there may have been some action between the two bodies, and Mr. Stanton noticed the fact that the copper became very brittle. It is possible that with pure gases not acting chemically on the electrodes no discharge at all takes place, but this is by no means proved, and on the whole I think the evidence is against the supposition. We must for the present be satisfied with the fact that we can actually trace the effect of chemical action in destroying the leakage of negative electricity.

Behaviour of Platinum Electrodes.—We owe to Messrs. Elster and Geitel* a series of most instructive experiments, in which they have discussed the unilateral conductivity of gases in several cases. Their research was chiefly directed to an investigation of some observed electromotive forces between glowing bodies and the surrounding gas. These electromotive forces, as well as those discovered by Righi, which appear under the action of ultra-violet light, will, I believe, prove to be of the greatest importance in clearing up many electrical questions, for they seem to me to belong to a class of phenomena which can be brought under the domain of the second law of thermodynamics. I am, however, for several reasons, anxious to avoid, for the present, a discussion regarding them, except in so far as they seem to have a bearing on the question of a possible chemical action at the electrodes. The facts discovered by Elster and Geitel are briefly as follows:—

If a white-hot platinum wire and a cold metal are brought near each other in an enclosure filled with gas at various pressures, a difference of potential is observed between the two metals; when the gas is air or carbonic acid, the hot platinum is electro-negative to the cold wire, while in hydrogen or hydrocarbons the opposite is the case. It is also found that platinum in air discharges positive electricity more readily than negative, while again the opposite is the case in hydrogen.

Messrs. Elster and Geitel bring these facts into connexion with each other. The curious relationship between unilateral conductivity and electromotive force, which they have traced, is an important one, but may only be one of those reciprocal relations (Peltier effect and thermo-electric force) so often met with in all parts of physics. As regards the explanation of these phenomena, several considerations occur to me which should make us careful not to pronounce a definite opinion at present. The authors take it for granted that the electromotive force has its seat at the hot junction of metal and air. That is probable, but it will be safer for the present not to commit ourselves to more than is actually observed, namely, that if a cold platinum wire in air is placed near a hot platinum wire, the hot wire will be electro-negative towards the cold metal, while in hydrogen it will be electro-positive. At first sight the behaviour of platinum wire seems exactly the reverse to that of copper; but platinum shows some curious effects on long continued heating, which lead me to the opinion that complicated effects here determine the nature of the phenomenon. Elster and Geitel have examined the changes in the behaviour of a platinum wire kept glowing in hydrogen. Two platinum wires were kept in the same enclosure; one of them was

* 'Wiedemann, *Annalen*,' vol. 19, p. 588 (1883); vol. 31, p. 109 (1887); Vienna Academy '*Sitzungsberichte*,' vol. 97 (Abth. 2. a.), p. 1175 (1888).

heated only during as short a time as possible, while the other was kept glowing for several hours. The former, while hot, became electro-negative towards the gas in contact, while the latter became electro-positive. It seems probable that the difference is due to gases dissolved in the platinum and given up by long-continued heating, and we are led to the opinion that in the normal state of platinum, when it is freed from its dissolved gases, it becomes electro-negative on heating. The authors do not state whether the unilateral property of hot platinum altered together with the sign of its electrification, though their own experiments would lead one to think that this was the case.

It is unnecessary to enter into the question how the dissolved gases can affect the result. We observe very similar phenomena with platinum electrodes in liquids. The great differences observed, owing to comparatively small changes in the state of the platinum, incline me to a chemical, rather than to a physical, explanation. An important experiment bearing on the question is worth quoting. Berliner* showed that the disintegration of platinum electrodes, so commonly observed in vacuum tubes, altogether ceases when the metal has been deprived of its dissolved gases. While disintegration is taking place the surface is constantly renewed, and any surface action between the platinum and the surrounding gases could be kept up continuously, but would stop as soon as the disintegration itself has stopped.

Similar effects to those described by Elster and Geitel had been previously observed by Goldstein and Warburg. After Hittorff† had discovered that the fall of potential at the negative electrode, which is necessary to produce a continuous discharge, disappears if a glowing platinum wire is taken as kathode, Goldstein found that the platinum wire permanently loses the power of acting if it is kept red-hot for a sufficient time. Warburg‡ states that, on hardening the wire by drawing it may be brought back to its original condition, so that on heating it will again discharge negative electricity freely. But I learn from private information which Professor Warburg has been kind enough to supply me that the surface of his wire might have become coated with greasy matter in the act of hardening, and, if that is so, we are at liberty to connect the free discharge of negative electricity with a chemical action at the electrode.

Behaviour of Carbon Electrodes.—It is clear that the behaviour of carbon electrodes cannot give us any certain information on the question as to how far unipolar effects depend on chemical action; but, as some phenomena shown by glow lamps have received the attention of electricians, it may be useful to point out that, as far as

* 'Wiedemann, Annalen,' vol. 33, p. 289 (1888).

† 'Wiedemann, Annalen,' vol. 21, 1884.

‡ 'Wiedemann, Annalen,' vol. 31, p. 592 (1887).

I can see, they present no special features which are not easily explained by well-known facts of vacuum discharges. Owing to the incandescence of the filaments, the different potential at the ends is sufficient to produce a discharge through the residual gas; hence the observed disintegration of the negative end of the filament. If a separate metallic plate is inserted into the lamp, its potential will be intermediate between that of the positive and that of the negative pole. On being connected with the positive pole a current will tend to pass in such a direction as will make the plate an anode. The current actually will pass, because we know that a conductor offers no difficulty to the discharge of positive electricity into a gas in which the discharge is established. This phenomenon has been called the "Edison effect." If the plate is connected with the negative electrode, it will tend to become a cathode. The fall of potential required is now much greater, and hence the current is much weaker, and may escape detection.*

According to the theory of electrolytic convection, we conclude that when an electrode is raised to a red or white heat the molecules partially dissociate and render conduction possible. It does not necessarily follow that the temperature alone is sufficient to dissociate the molecules; it may be that the addition of an electric stress is necessary. It will be a matter for future investigation to decide whether the decomposition goes on at the same rate in contact with a negative wire as it does in contact with a positive wire.

2. *Behaviour of Electrodes illuminated by Ultra-violet Light.*—Hertz,† during his celebrated experiments on electric oscillations, noticed that a spark passed more easily between metallic points when these were illuminated by a simultaneous strong spark from another source, and traced the effect to the illumination of the secondary electrodes by the ultra-violet rays sent out by the primary spark. Messrs. E. Wiedemann and Ebert‡ found that the negative electrode only is active in this case, and Hallwachs§ subsequently attacked the question by a method which has yielded very interesting results.

He connected a gold leaf electroscope with a clean plate of zinc, upon which a beam of strong ultra-violet light was allowed to fall. The zinc was found to be incapable of retaining a negative charge; the effect on a positive charge was so small that at first sight it seemed totally absent. But the fact to which I wish to draw special attention is the importance, in order to ensure the success of the experiment, of taking a clean surface of zinc. Hallwachs found that

* [All the facts described by Mr. Fleming in his recent communication ('*supra*, p. 118) will be found to agree with this explanation.—May 30.]

† '*Wiedemann, Annalen*,' vol. 31, p. 983 (1887).

‡ '*Wiedemann, Annalen*,' vol. 33, p. 241 (1888).

§ '*Wiedemann, Annalen*,' vol. 33, p. 301 (1888).

zinc exposed to the air for some time showed the negative leakage to a much smaller extent, but the positive leakage was not affected, so that old surfaces sometimes discharged a positive charge more easily than a negative one. Other metals behave like zinc, but the less oxidisable ones show the effect to a much smaller extent.

Hallwachs draws the conclusion, to which indeed his experiments seem inevitably to lead, that the ultra-violet light produces a chemical change at the surface, which is of the same nature as the one going on when surfaces are left lying exposed to the air. The explanation which at first sight seems the most natural one, namely, that the chemical change is an oxidation, would appear from an experiment more recently communicated by him* not to be the true one, for copper covered with a film of oxide behaves like clean metallic copper.

Shortly after the publication of these experiments, Righi† showed that a photo-electric air-cell can be constructed by taking two parallel plates of different metals with an air space between them and connecting them with each other. If one of the plates is of zinc, the other of brass, and if the zinc plate is illuminated, a current tends to flow from the zinc to the brass through the air.

In the actual experiments, the brass plate was in the form of a wire netting, so that the rays from an arc lamp could pass through the grating and fall normally on the zinc plate, and the difference of potential was observed by means of an electrometer. The energy of ultra-violet light vibrations must therefore directly or indirectly be converted into that of electric separation, and it is to my mind natural to assume that a chemical action is set up in the first place by the light, and that the observed electrical effects are therefore in the first instance due to chemical action. The fact that the electromotive force of such a photo-electric cell is in the same direction as if the plates were immersed in water, the zinc becoming the anode, is very suggestive. At present, however, we must not attach too great an importance to it. I consider it quite possible that if the oxygen of the air is replaced by hydrogen, the currents would still be in the same direction. Stoletow‡ has examined the intensity of currents sent from an outside electromotive force through an interval between two parallel plates acting as electrodes, the kathode being illuminated by ultra-violet light. I cannot at present attach any very great importance to the experiments made with different gases. We know how very delicate the surface actions on which these currents depend are, and how the greater part of the effect may in some cases be due

* 'Wiedemann, Annalen,' vol. 37, p. 666 (1889).

† 'Phil. Mag.,' vol. 25, p. 314 (1888).

‡ 'Comptes Rendus,' vol. 107, p. 91 (1888).

to small traces of foreign gases or to the state of surface of the electrode.

The modifications of the disruptive discharge between platinum electrodes, which have been studied by Wiedemann and Ebert,* deserve to be mentioned, but they depend on too many circumstances to help us in deciding the question as to the possible effects of chemical action at the surface of the electrodes. In order to obtain an insight into these questions, it seems better to study the discharges produced by radiation in cases where naturally a discharge would not occur. This will probably lead to a simpler result than an investigation of the modification by radiation of a discharge independently produced. The interesting facts discovered by Lenard and Wolf will be mentioned in connexion with another part of our subject.

Discharges through Flames.

It was discovered by Paul Erman† towards the beginning of this century that a flame may conduct, and that a wire placed inside it discharges positive electricity more easily than negative electricity. Buff‡ found that even the gases rising from a flame behave as conductors of electricity, and Giese has carefully examined the behaviour of these gases. He was thereby led, as has already been mentioned, to the theory of electrolytic convection. It seems indeed impossible to draw a different conclusion. We may assume that in a flame a certain proportion of dissociated ions are present, some of which can escape combination with each other for some time. As the gases rise from the flame they will remain conductors until the recombination of ions is complete, and this may take some time. According to Giese, the gases may preserve their conductivity for some minutes.

Dissociation alone, it must be remembered, is not sufficient to convert a gas into a conductor. Thus, when owing to increased temperature the molecules of iodine vapour split up, the atoms do not necessarily behave as ions, for they are probably unelectrified. We must imagine each iodine atom in the molecule to possess two charges, and as dissociation proceeds a re-arrangement of the charges takes place, so that the free atom will still carry two equal but now opposite charges.

Discharge through Gases in the Sensitive State.

It is convenient to say that a gas is in its sensitive state as regards electric stress when any electromotive force, however small, pro-

* 'Wiedemann, *Annalen*,' vol. 33, p. 241 (1888).

† 'Gilbert, *Annalen*,' vol. 11, p. 150 (1802).

‡ 'Annalen der Chemie,' vol. 80, p. 1 (1851).

duces a transference of electricity. I have shown that a discharge, whether disruptive or continuous, throws the whole enclosure into a sensitive state. It has been suggested from various sides that some of the phenomena described by me were due to illumination of ultra-violet light. In order to decide the question, I have divided a vacuum tube into two parts by means of a quartz diaphragm; a discharge passed through one part of the tube and on that side the effects previously described by me were again observed, but the quartz plate completely destroyed the effect in the other compartment, while all observers agree that quartz is transparent to the radiations which produce electrical effects.

Because E. Wiedemann* finds (in accordance with Hallwachs' experiment) that the leaves of an electroscope can be made to collapse when they are illuminated by an arc lamp, it hardly follows, as implied by him, that this is the explanation of the same effect observed by me when there was no arc lamp nor any light except the feeble glow of a discharge carefully screened off from the gold leaves by a metallic plate. The above-mentioned experiment, which will be described in detail in another communication, disposes of the question, and shows that, independently of any ultra-violet radiation, the discharge puts the gas into a sensitive state in which it becomes a conductor. According to the theory of electrolytic convection, this should be so, because the primary discharge supplies the necessary ions.

Discussion of Unipolar Effects.

It is of interest to see whether we can trace any regularity in the appearance of the unipolar effects, and whether there is any hope of a general law which will allow us to predict when an electrode will be positively, and when it will be negatively, unipolar.

I am aware of the dangers of premature generalisation, but, at the same time, such generalisations as a rule do no harm except perhaps to the reputation of the author; they have, on the other hand, the advantage of putting the issue clearly before the reader, and often lead more quickly to a definite result than a mere statement of disconnected facts.

As far as the facts go at present, I am inclined to draw the following conclusion:—*A free discharge of electricity between a negative ion and the anode is possible. On the other hand, a considerable fall of potential is required in order to produce an exchange of electricity between a positive ion and the kathode unless the electrode takes part in a chemical action set up at its surface, in which case the rate of exchange of charges at the kathode may become greater than that at the anode.*

* 'Wiedemann, Annalen,' vol. 35, p. 219 (1888).

A word is necessary to explain what I mean by a considerable fall of potential at the electrode. In electrolytes the fall of potential within the double layer is of the order of magnitude of 1 volt; such a fall in itself would hardly make itself apparent in our measurements in gas discharges. The observed fall of potential in vacuum tubes at the kathode is measured in hundreds of volts, but it will appear that within molecular distances the fall is many times smaller than for electrolytes, so that the normal force at the kathode may be less in gases than in electrolytes. The difference between an electrolyte and a gas is this: that, while in a liquid the fall of potential only takes place within a molecular range, in the gas it continues through a measurable distance. The cause of this, no doubt, has to be explained, and an attempt will be made to do so. At present it is sufficient to point out that a large fall of potential within, say, a centimeter of the electrode is not inconsistent with the much smaller fall observed within the double layer of liquids. It must also be kept in view that all measurements of potential in the gas are made by means of secondary electrodes. If a double layer of the same moment covers both the kathode and the secondary electrode, it would escape detection. There are some delicate questions involved in this which will be discussed in the complete paper. The main conclusions drawn in the text are not altered by the fuller discussion of the problem. A few facts may be quoted in support of the view I have taken concerning the effect of chemical action at the kathode. A flame conducts, because in the flame the molecules are broken up by independent chemical action; we find, in consequence, that an electrode can freely discharge positive electricity. On the other hand, a glowing piece of charcoal may act as electrode, because it takes part in a chemical action, but it is the negative electricity which now escapes freely.

In a vacuum tube, whatever chemical action may take place at the kathode diminishes the fall of potential, as appears from Warburg's* observations, who finds that electrodes of zinc and copper in hydrogen, when first introduced and therefore probably covered with a film of oxide, show a considerably smaller fall of potential than after they have been used some time, when the oxide film may be supposed to have been removed. In a similar manner a small admixture of moisture in nitrogen tubes, causes a considerable reduction in the fall of potential. As regards red-hot copper wires, we have seen that the passage of negative electricity from the electrode to the gas for small electromotive forces may be prevented altogether, if chemical action is prevented, while the electrode may still act as anode. Here it is the combined effect of temperature and electric stress that splits up the molecules into ions.

* 'Wiedemann, *Annalen*,' vol. 31, p. 592 (1887).

Finally, the action of ultra-violet light, being probably of the nature of a chemical action, at once destroys the impediments which prevent metals acting as kathodes. The principal difficulty of the explanation lies in the behaviour of white-hot platinum in hydrogen, but, as has already been explained, the platinum seems to undergo a molecular change in that case, which may either be due to or equivalent to a chemical action.

Properties of Gases in their Sensitive State.

A gas may be put into a sensitive state when the molecules are broken up into ions either by a discharge of electricity or by a chemical action as in a flame. It is interesting to note the similarity of behaviour of gases made sensitive in these two ways.

In a footnote to the paper, in which the theory of electrolytic convection is brought forward by Giese, he suggests that the power of gases rising from flames to condense moisture, as shown by Aitken, may be due to the same cause as its power to conduct electricity. The question has been treated with great ability by R. v. Helmholtz, whose untimely death at an early age science has recently had to deplore. R. v. Helmholtz was led to the enquiry by the discovery of an effort of electric discharges to act in the same way as solid nuclei would in precipitating the aqueous vapour from a moist gas. It would seem natural at first sight to ascribe this effect, as well as those previously described by Aitken, to the actual presence of dust particles. I must refer the reader to Helmholtz's paper,* in which this hypothesis is finally found to be insufficient and in which the action of both flames and electric discharges is ascribed to the presence of ions in the gas. Messrs. Lenard and Wolf† have recently shown that when a metal, charged negatively, is exposed to ultra-violet light, the space in front of the discharging plate acts on a steam jet like dust particles would. They conclude from these researches that the ultra-violet light does actually disintegrate the surface of the conductor. Some of their experiments, however, admit of a different interpretation; the electric discharge itself, which we know to take place under the circumstances, might be the cause of the condensing power of the air. As far as the evidence goes, I should say that the explanation given by Lenard and Wolf is the more probable one, though it is not altogether proved as yet. But even admitting the presence of dust particles thrown off from the conductor, it is still an open question whether the disintegration of the electrode is the *cause* of the electric discharge or whether it is only one of the phenomena attending it. We should expect a con-

* 'Wiedemann, Annalen,' vol. 32, p. 1 (1887).

† 'Wiedemann, Annalen,' vol. 37, p. 443 (1889).

siderable amount of energy to be required to convert the metal surface partially into dust, and it seems doubtful whether the mere absorption of ultra-violet light is sufficient for the purpose. If the action of the light is primarily a chemical one, the disintegration might be explained, like the discharge itself, as a consequence of this chemical action.

The fact that flames behave as diamagnetic bodies has long been known, and could be explained if we were free to assume that ions are diamagnetic. From the point of view of Weber's theory of diamagnetics, this seems probable, and I made a few experiments in order to prove in other ways the diamagnetism of ions. I have not hitherto obtained decisive results, but some effects of magnets on the discharge described in my previous Bakerian Lecture seem to me to point directly to such a diamagnetism.*

From the point of view, then, of our theory, a gas is sensitive electrically when it contains free ions. On the other hand, we must conclude that when a gas is not sensitive such free ions are not present. I do not see how the insulating power of air at the ordinary temperature is consistent with the presence of ions, however few in numbers; for, ultimately, a diffusion to the electrodes and a discharge would necessarily take place. This seems to me to be fatal to J. J. Thomson's view of the disruptive discharge.†

The Continuous Discharge.

Facts hitherto established.

The first step towards the investigation of the continuous discharge is the investigation of the relation between current and fall of potential in a gas through which a current is passing. An important fact discovered by Hittorf‡ relates to the fall of potential in the positive part of the discharge, that part which extends from the anode towards the negative glow. Hittorf's law may be stated as follows:—

"In the positive part of the discharge the rate of change of potential at a given pressure is independent of the current."

The law was tested by Hittorf with currents which differed in intensity nearly in the ratio of 1 to 50.

As regards the negative glow, Hittorf chiefly experimented with electrodes in the form of wires running parallel to the axis of his tubes. The glow for weak currents only covers the ends of the electrode, but as the intensity is increased it gradually extends backwards; during this stage the rise of potential near the kathode

* 'Roy. Soc. Proc.,' vol. 37, p. 317 (1884).

† 'Phil. Mag.,' vol. 15, p. 427 (1883).

‡ 'Wiedemann, Annalen,' vol. 20, p. 705 (1883).

is independent of the current. When the glow has completely covered the kathode, a rise in the intensity of the current is accompanied by an increased difference of potential between the kathode and the surrounding portions of gas.

Warburg* has studied the fall of potential near the kathode with electrodes made of different material and at different pressures. It is known that the negative glow consists of three parts: a luminous layer directly adjacent to the kathode, the so-called dark space, and the glow proper. As the density of the gas diminishes these layers gradually expand; but the difference of potential only changes slowly. It has been stated that the difference of potential between a kathode which is not completely covered with the glow and some point in the glow is independent of the intensity of the current; Warburg calls it the normal fall of potential. While the fall is normal a change of current is only accompanied by a change in the extent to which the kathode is covered with the glow. Warburg has shown how the normal fall depends on the material of the electrode, the nature of the gas, and the density, and his results are of considerable interest from our point of view. Slight quantities of moisture added to nitrogen produce a considerable change in the difference of potential. Thus, with platinum electrodes nitrogen containing a small quantity of aqueous vapour gave a normal fall of 260 volts, while dry nitrogen gave 410 volts. This is not due to the fact that aqueous vapour is a better conductor than nitrogen, for, if more than traces of moisture are present, the fall of potential is as great or greater than with dry nitrogen. We must, on the other hand, find in these observations a strong support of our view, that the difficulty of passage of positive electricity from the gas to the electrode is much reduced by chemical actions at the electrodes. The effects of small traces of moisture are so similar to those investigated by Dixon and others in chemical reaction between gases and between a solid and a gas, that in my opinion we really have no choice but to adopt some such view as I have taken of the matter. Warburg draws the same conclusion from his experiments.

The effects of deoxidation of the electrodes, where zinc or steel kathodes are used in hydrogen, makes itself apparent by considerable reduction of the fall of potential near the kathode, which disappears when the layer of oxide on the kathode has been removed by disintegration of its surface. A change of pressure, according to Warburg, is only accompanied by a slight change in the normal fall of potential.

* 'Wiedemann, *Annalen*,' vol. 31, p. 592 (1887).

Volume Electrification near the Kathode.

I have spent considerable time during the last few years in investigating the fall of potential in the different parts of the negative glow with a view to deciding whether there is any considerable volume electrification of the gas itself.

De la Rue and Müller* have already endeavoured to measure the potential at different places in the dark space; but for some reason, which I cannot trace, their results are altogether anomalous. They used what they call four different arrangements of leads, which, however, all should give identical results; but no regularity can be traced. In many cases they found that the potential becomes more and more *negative* away from the kathode, so that in one of their observations some point in the dark space was at a potential -1068 volt, the negative electrode being at potential zero. I have never observed anything but a regular increase of potential within the dark space. In order to be able to subject the results of experiments to a simple analysis, I have used two different kinds of vessel. In one the lines of flow were, throughout, parallel to each other; this I shall call the axial discharge. Cylindrical tubes were used, and the kathode was a closely fitting aluminium plate, care being taken to prevent a discharge from the back. The other vessels used were large cylindrical receivers, the kathode being a wire forming the axis of the cylinder, and the anode a cylinder made of wire gauze. The lines of flow in these vessels were radii drawn from the axis of the cylinder, and I shall call the discharge in this case the radial discharge. The fall of potential between the kathode and any point inside the negative glow was found to be capable of being represented by the formula

$$V = V_0(1 - e^{-\kappa x}) \dots\dots\dots (1.),$$

where V is the potential at any point, V_0 the potential in the glow proper, κ a constant, and x the distance from the kathode. The potential of the kathode is taken as zero. The formula is not meant to be more than an approximate one, but within the limits of error of experiment the formula may be taken as correct through the dark space and the inner parts of the glow. It may, in the first place, only be considered as an interpolation formula, and others might be found representing the facts equally well, but the equation gains some reality owing to the fact that κ for a given pressure is found to be very nearly independent of the strength of the current. The complete account of my experiments will show how far this is correct. Owing to the circumstances of the case, the fall of potential

* 'Phil. Trans.,' 1883 (vol. 174, p. 477).

could not be altered more than in the ratio of one to two, and it is not possible to tell, therefore, how far the above will express the results for a greater change in the current density. The constancy of κ depends on the fact which I have verified within these limits of currents, that *the potentials at different points of the negative glow all rise and fall in the same ratio when the current is altered, the kathode being at zero potential.*

From the characteristic equation for the potential, which in our case reduces to

$$\frac{d^2V}{dx^2} = -4\pi v^2\rho,$$

in which v stands for the velocity of light, we may now deduce ρ , or the volume-density of electricity near the kathode.

The law which I have given above suggests at once that ρ is a linear function of V or its differential coefficients, for it implies that if V is any solution of the characteristic equation, λV must also be a solution. The question will be discussed in the complete account of these experiments, and it is not necessary to enter into it here. From equation (1) we derive

$$4\pi v^2\rho = \kappa^2 V_0 e^{-x\kappa} \dots\dots\dots (2.),$$

which shows that *the kathode is covered with an atmosphere of positively charged particles diminishing outwards in volume-density.*

The law of variation of density is the same as that found in the atmosphere near the earth's surface; but the mathematical conditions are very different. The gravitational force near the earth is sensibly constant, while the electrical forces near the kathode vary as much as the density.

If the curve which connects V and x is plotted, its curvature, and therefore the electrification, can be traced through the dark space and into the negative glow, but inside the glow it rapidly diminishes. The formula for ρ does not lay claim to more than an approximate expression of the facts, which may, however, in default of more accurate knowledge help us to form some idea of the distribution of volume-density. Even though (1) may hold with considerable accuracy, (2) may not give correct results for those parts of the glow which are close up to the electrode; for the curve representing V near the origin is a very steep line, slightly curved. A small change in the curvature will make a considerable change in ρ , without affecting the main curve to an appreciable extent. It seems probable, however, that the electrification continues to increase up to the electrode itself, and that the formula will express the main features of the distribution. When the lines of flow are radial the law of distribution of volume-density is less simple, but the general result is the same.

It is interesting to gain some idea of the charges in absolute units which are involved, and of the number of charged ions taking part in the discharge according to our theory. The electrification at the surface according to (2) is $V_0\kappa^2/4\pi v^2$. In a series of experiments in which V_0 varied from 672 to 1330 volts, and the current between 400 and 3000 microampères, $\kappa^2 V_0$ was found to vary between 3×10^{12} and 10^{13} C.G.S. units. Taking the highest value, we find $\rho = 10^{-9}$ C.G.S. electromagnetic units, or about 30 electrostatic units. From this I calculate that the *mass* of electrified atoms per unit volume is 7×10^{-13} , on the supposition that the charges are carried by nitrogen-atoms. The density of nitrogen in the experiment which forms the basis of this calculation is 5×10^{-7} , so that even close up to the electrode the surplus of positive ions is very small compared to the number of atoms and molecules present, only about one molecule in a million being decomposed. Further away from the kathode the relative amount of charged to uncharged particles is considerably smaller still. The volume-density, which is derived from calculation, gives us, of course, the difference only between the sum of the positive and the sum of the negative charges. The value of this excess of positive charges cannot therefore be taken as a measure of the total number of ions present, except perhaps close up to the electrode. In how far the positive charges in the polarising layer and the negative charges projected away from the kathode are *alone* sufficient to account for the whole current, cannot be decided at present. The mutual repulsion of the particles within the atmosphere of positive particles which surrounds the kathode explains at once the tendency of the glow to spread all over the surface of the electrode. Other important facts, such as the effects of an anode near the kathode in driving away the glow, will also find their natural explanation. The spreading of the glow over the negative electrode is the cause of a series of peculiar differences which appear at the two poles even in the case of discontinuous discharges. The differences observed in *Lichtenberg's* figure and in *Priestley's* rings, according as the discharging point is positive or negative, seem to me to be readily explained by the atmosphere of positive ions which always tends to spread all over the kathode, while the discharge from a positive electrode is confined to the points of maximum electric density. It will lead me too far to enter into these questions here; but one objection must be met: why does this positive electrification not make itself apparent by electrical action in the space outside; and why do electrified bodies outside not act on the glow?

As regards the first question, the charge is not really a large one. The whole quantity of electricity in the glow per square centimeter cross-section would, according to the formula, be—

$$\frac{dV}{dx} / 4\pi v^2,$$

where dV/dx stands for the fall of potential at the kathode. In my experiments this quantity has been smaller than 10^{12} C.G.S., so that the maximum total charge per centimeter cross section would amount to about three electrostatic units. The effect of this electrification would be completely hidden by the charges on the outside of the glass tube, which cannot be avoided when we are dealing with a thousand volts. In fact, the leakage over the glass will act as an electrical screen.

It also appears that electrified bodies outside cannot produce any effect on the inside of the tube, because it can be shown from my previous work that the surface conditions in the interior of a gas through which a discharge passes render a normal force at the surface impossible. Hence no lines of force can pass from the outside to the inside. If an electrified body is approached, a momentary redistribution of the surface charge inside the vessel will take place; but after the readjustment no further effect can be observed.

It is generally stated that a greater electromotive force is required to start a discharge than to maintain it after it is once started. This statement requires qualification. The fall of potential in the positive part of the tube is of course much smaller during discharge than it was just before, but it does not follow that the rate of fall at the negative electrode is less. In one experiment the rate of fall at the kathode at a pressure of 6 mm. was 9000 volts per centimeter, while the whole of my battery only had a difference of potential of less than 2000 volts. According to De la Rue and Müller, it requires a fall of about 1800 volts to start a discharge between two parallel plates at a pressure of 10 mm. Their measurements do not extend to smaller pressures, but a discharge would be started at the pressure of about $\frac{1}{2}$ mm. by a less electromotive force than at a pressure of 10 mm. It follows that while the discharge is passing, in most if not in all my experiments, the fall of potential was much greater than that required to start it, and if we adopt the view that the breaking down of the insulation is in part due to a decomposition of the molecules, it follows that the molecules must continue to be decomposed during the discharge. This we shall find to be a result of importance.

The charge on platinum electrodes in liquids is much greater than the charge on the surface of the kathode in a gas; with the usual data I make it about 10,000 times greater. This would explain the absence of observable polarisation in the case of the gas discharge, but it seems surprising that any electricity should pass at all under the circumstances, between the gas and the electrode. My calculations, however, depend on the extension of an experimental formula

up to the electrode, which may not be justifiable; but another explanation is possible. If we ask at what distance from the kathode is the potential 1 volt less than at the kathode itself, we find it to be about the thousandth part of a millimeter. It will constantly happen that particles will approach the kathode from that distance, and the work which has to be done in the transference of the positive ion to the electrode may be partially supplied by the energy acquired in the fall.

Effect of a Magnet on the Negative Discharge.

Confirmation of the Theory.

In my former paper I described a method by means of which I hoped to be able to measure the charges carried by the ions, and thus directly to test the truth of the theory. It is clearly most desirable that this should be done, for if it could be shown that the molecular charges are the same as those carried by the atoms in electrolytes, all further doubt as to the correctness of the view which I advocate would vanish. I have met with very considerable difficulties in the attempt to carry out the measurements in a satisfactory manner, and have only hitherto succeeded in fixing somewhat wide limits between which the molecular charges must lie.

According to one theory, particles are projected from the kathode. The observed effect of the magnet on them is exactly what it should be under the circumstances. The path of the particles can be traced by means of the luminosity produced by the molecular impacts. If the trajectory is originally straight, it bends under the influence of a magnet. The curvature of the rays depends on two unknown quantities, the velocity of the particles and the quantity of electricity they carry.

If the particles carrying a charge are moving with velocity at right angles to the lines of force, the radius of curvature r is determined by the equation

$$\frac{mv^2}{r} = Mve \quad \text{or} \quad \frac{e}{m} = \frac{v}{Mr} \dots\dots\dots (1.),$$

where m is the mass of the particle. If the particles originally at rest, start from the kathode at which the potential is taken as zero, and arrive, without loss of energy, at a place where the potential is V , we should have another equation, namely :—

$$2Ve = mv^2 \dots\dots\dots (2.).$$

Eliminating v , we find :—

$$\frac{e}{m} = \frac{2V}{M^2r^2} \dots\dots\dots (3.).$$

The quantity e/m thus obtained can be directly compared with the known electro-chemical equivalents. The assumption that in the passage of the particles, the whole work done appears as acceleration can never be perfectly realised, and experiments only can decide how nearly we may approach it. In the dark space surrounding the kathode the dissipation of energy is probably small, and we have every reason to believe that there the velocities are very high. I need not enter here into the many experimental difficulties which I have encountered, and which I hope soon to overcome more completely than I have yet been able to do. In the experiments hitherto carried on equation (2) cannot be assumed to hold. The equation (3) may be used, however, to fix an upper limit for e/m . A lower limit can be calculated as follows:—As long as the effect of the magnet on the particles projected from the kathode shows any directional preponderance, we may take it that the velocities of the particles must be greater than the mean velocity in their normal state. For it is clear that, if distribution of velocities was symmetrical in all directions, the magnet would have equal and opposite effects on the charges which move in opposite directions; and if by mutual impacts the velocity is reduced to its normal value, it will also have lost any directional inequality. We may obtain a lower limit for e/m if in equation (1) we calculate

$$\frac{e}{m} = \frac{v}{Mr} \dots\dots\dots (4.),$$

by putting for r the smallest radius of curvature which can with certainty be traced in the glow, and for v the mean velocity of the particle, according to the kinetic theory of gases.

In an actual experiment M was 200; r diminished with increasing distance from the kathode. The greatest value which could with certainty be measured was about 1 cm. V was 225 volts at the same place. Taking these numbers, we get for the upper limit

$$\frac{e}{m} < 11 \times 10^5.$$

In the glow the radius of curvature is quickly reduced to about $\frac{1}{2}$ cm., showing that the luminosity is directly due to a conversion of directional into thermal motion. The gas in the actual experiment was nitrogen much contaminated with hydrocarbons. The value of the mean velocity in the state of equilibrium will depend on the supposition we make as to the nature of the particle which carries the charge.

It will be sufficient to consider the cases indicated in the following table:—

Nature of particle.	Velocity of mean square.
Hydrogen atom.....	26×10^4
Hydrogen molecule	18×10^4
Nitrogen atom.....	7×10^4
Nitrogen molecule.....	5×10^4

As we are only dealing now with the order of magnitude, the temperature need not be taken into account, and we may take v to be 10^5 ; we thus obtain

$$\frac{e}{m} > 10^3.$$

The actual value of e/m is 10^4 for hydrogen and 0.7×10^3 for nitrogen, if we imagine each atom of nitrogen to carry the same charge as the atom of hydrogen in water; but, as nitrogen may unite with these atoms of nitrogen we must assume three charges at least to be carried, which would make e/m equal to 2×10^3 .

It thus appears that there is nothing in the actual facts which is in any way not in harmony with the theory. The lower limit for e/m comes very near the actually observed values, and it is not astonishing that the upper limit yields so great a value. It will be seen that in equation (3) the radius of curvature enters as the square. I think I may take the experiments hitherto recorded as a confirmation of the theory. Assuming the theory to be correct, they show that in the glow the particles are quickly reduced to a velocity of the same order of magnitude as the mean velocity in an unelectrified medium. If the particles do not carry fixed charges, they must become electrified by contact at the electrodes. This is the view generally taken, and it is interesting to trace its consequences. The change e of a sphere touching a plane charged with surface density σ is* given by

$$e = \frac{2}{3} \pi^3 a^2 \sigma = 20 a^2 \sigma \text{ approximately.}$$

Substituting for σ the highest value which I have obtained in my experiments, about 2.5 electrostatic units, e would be numerically equal to $50a^2$. If for a^2 we take about 5×10^{-10} , which is the molecular range obtained from experiments in gases, we should be above the mark. This, when substituted in the above, gives for e the value 10^{-17} in electrostatic units, instead of 10^{-12} , that is, the charge would be about 100,000 times less than according to our theory. Applying the equation (4), I calculate that, according to the hypothesis of electrification by contact, the average velocity of the molecules would only have been 2 cm. a second, which is a *reductio ad absurdum*.

* Maxwell, vol. 1, p. 257.

Some Questions relating to the Positive Discharge.

There is one theory of electric discharges which, as a scientific curiosity, is of interest. It asserts that a perfect vacuum is a perfect conductor, but that the molecules flying about the vacuum impede the passage of the current. If no discharge actually passes through highly rarefied gas in an experiment, it is, according to this view, because there is a resistance at the surface of the electrodes. It is interesting to speculate what the world would be like if this theory was true. It is perhaps not fair to urge that we should live in perpetual darkness, because the upholders of the theory could not consistently adopt the electro-magnetic theory of light, whose essence is a stress in the medium. But I do not see how we should have any electrostatic effects at all, at any rate in highly exhausted vessels. In order that gold leaves should remain divergent *in vacuo*, it is by no means necessary that no escape of electricity should take place from them. They will collapse, though their surface may be perfectly impermeable to the discharge, as long as currents may flow in the surrounding medium. If the gold leaves are charged positively, negative electricity would flow towards them, cover them, and protect the leaves, so as to prevent any repulsion. There are other fatal objections against the theory which will survive nevertheless, for, like all paradoxes, it has an irresistible attraction to a great many minds.

The following experiment has convinced those to whom I have been able to show it that the discharge consists of a diffusion of charged atoms or molecules. The apparatus used is that by means of which Balfour Stewart and Tait have carried on their researches on the heating of a rotating disc *in vacuo*. In front of an ebonite disc, electrodes were introduced so that the line joining them was parallel to the plane of the disc, viz., one electrode opposite the centre, and the other opposite the edge of the disc. When the latter is rotated, it carries round with it the air in its neighbourhood. If the current consisted of a motion of the medium, the particles of air could not affect the distribution of the lines of flow. But it is found that the discharge is drawn up or down according as the motion of the air is upwards or downwards. The curves formed by the discharge are similar to those observed when a magnet acts on a positive discharge, and their cause is identical, as the magnetic force also acts on the particles, and tends to draw them through the discharge, as I have explained in my previous Bakerian Lecture.

Photographs of the actual appearance have been taken, and will be given in the full account of these experiments. It is very striking to see the discharge steadily and slowly deflected by the rotating disc, and so sensitive is it to slight currents in the air, that the heating of the gas by the discharge and the convection currents formed in

consequence are quite sufficient to cause a decided bending, even without any rotation of the disc.

Magnitude of some of the Quantities involved in the Discharge.

As it is necessary to bear in mind the order of magnitude of some of the quantities involved in the discharge, I may briefly note some of the most important ones.

The most probable value for the charge carried by each atom of hydrogen I find to be 3×10^{-23} electro-magnetic units, more generally, say, $3\kappa \times 10^{-23}$ where κ is a numerical constant.

Question I:—How does the energy acquired by an ion between two impacts compare with the average kinetic energy of a molecule?

Answer:—The ratio e/m for hydrogen is known to be 10^4 approximately. If a particle of mass m carries a charge e , the velocity generated from rest through a range in which the difference of potential is V is

$$\sqrt{\frac{2eV}{m}} \quad \text{or} \quad 140 \sqrt{V}.$$

If V is one volt, this would be equal to 14×10^5 ; a quantity nearly ten times as great as the mean velocity of a hydrogen molecule. In the positive part of the discharge when the velocity of diffusion is uniform, the fall of potential in my experiments was, roughly speaking, about 1 volt per millimeter; the mean free path calculated according to the kinetic theory varied between $\frac{1}{2}$ mm. and $\frac{1}{4}$ mm. Hence, on the average, the velocity generated in the atom by electric forces between two encounters exceeds several times the mean velocity in the stationary state. It will appear that the number of atoms carrying charges is small compared to the total number; so that the actually observed rise in temperature need not be considerable. At each impact the atom must give up, on the average, that proportion of its own velocity which it gains during two encounters; and the above numbers show that the energy communicated is very considerable. Hence the luminosity of the positive discharge. Even if by an impact the ions are thrown back, the electromotive force will, in general, be strong enough to reduce it to rest, and send it forward before the next impact. The path of particles will therefore not be straight, and the velocity of the ions before impact will almost entirely be in the direction in which the force acts.

Question II:—If the molecules, each charged with a quantity of electricity e , approach each other with a velocity equal to the mean speed in a homogeneous gas at ordinary temperature, at what distance from each other will they come to rest?

Answer:—If v is taken as 17×10^4 , and $e = 3\kappa \times 10^{-23}$, the distance is $2\kappa \times 10^{-8}$, which is larger, though not considerably so, than the molecular distance. We conclude that two particles charged with the same kind of electricity will, in general, not approach each other sufficiently near to bring other than electrical forces into play.

Question III:—At what distance is the force between two equally charged atoms equal to the force in a field in which the fall of potential is 1 volt per centimeter?

Answer:— $r = \sqrt{3\kappa} \cdot 10^{-5}$. If the fall is 1 volt per mm., the distance would be three times as great, or about 5×10^{-5} .

Question IV:—What is the proportion of ions amongst the molecules in the positive part of the discharge?

Answer:—I assume, as a first approximation, the velocity of diffusion to be that of the mean velocity of the gas in the normal state. (One measurement of the magnetic deflection in the glow shows that the velocity of diffusion cannot be much greater, and the answer to Question II shows that it cannot be much smaller.) If S is the cross-section of the tube, C the current, and n the number of ions, we have

$$nSev = C; Nm = \rho,$$

where N is the number of undecomposed molecules, and ρ the density of the gas. Combining the two equations:

$$\frac{n}{N} = \frac{mC}{S.e.v.\rho}.$$

In a typical example, ρ was 5×10^{-7} ; $C = 3 \times 10^{-4}$; $S = 2$; and as $\frac{e}{m} = 10^4$, we find

$$n/N = \frac{1}{5} \times 10^{-6},$$

a small fraction, which is suggestively near the fraction obtained for the proportion of positive ions in close contact with the kathode; the two results being observed from altogether different quantities.

Question V:—What is the average distance between the ions in the positive part of the discharge?

Answer:—With the same data as in Question IV, I find for the average distance approximately 10^{-2} , or $\frac{1}{10}$ mm.

*Probable Explanation of the Fall of Potential observed at the
Kathode.*

In carrying out the investigation of which the experiments described in this paper form a part, I have always attached most

importance to the clearing up of those questions on which the mathematical analysis of the subject will have to be based. From this point of view, nothing is of greater importance than the investigation of the surface conditions which must hold between the gas and the vessel, and between the gas and the electrodes. In a previous paper,* I have shown that at any part of the surface of the gas through which no electricity passes the normal forces must vanish, which is not *a priori* evident, if we consider the gas to possess a certain dielectric strength. The fall of potential at the kathode must depend on the surface conditions which hold there, and the following considerations may help to clear up the question.

Imagine, in the first instance, a gas containing a certain number of charged particles, and enclosed in a vessel kept at zero potential, but having a surface impermeable to electricity. We may not be able to realise these conditions, but we may discuss the problem as an ideal case.

How will the charged particles arrange themselves under the influence of their mutual forces? They will, no doubt, travel outwards towards the surface, but will they cling to the surface, condensing, as it were, to form a layer against the solid surface resembling a liquid more than a gas? Or will they form a gaseous atmosphere, diminishing in density from the surface outwards? Or, finally, will they resemble the state of a liquid in contact with a gas, that is to say, will they be in a state of movable equilibrium, a certain proportion always clinging to the surface of the solid, others flying away until brought back by impacts and electric forces? I do not see how the answer to these questions can be given on the theoretical grounds only, and it seems to me that experiment only can decide it. Nor is it necessary, to my mind, that an atmosphere of positive ions should behave exactly in the same way as an atmosphere of negative ions. The only consistent theory of contact electricity we possess is that worked out by Helmholtz, according to which we must, in calculating the work done in the transfer of electricity through a surface, not only take account of electric but also of electro-chemical forces. There are various ways of expressing the same fact. We may say that there must be a definite attraction between matter and electricity, or we may say that the potential energy of a system contains terms involving both electrical and chemical variables, or, finally, that both chemical and electrical forces are due to stresses in the medium, and that in calculating the forces we must add the displacements and not the energies.

In considering the mutual action between electrified particles at molecular distances, it is quite possible, and even probable, that positive and negative electrification may affect the molecular forces

* 'Roy. Soc. Proc.,' vol. 42, p. 371 (1887).

in different ways. The same holds as regards the action between electrified and non-electrified particles. If the theory of electrolytic convection in gases is true, some hypothesis of this nature is necessary to explain the asymmetry of the discharge. Positive ions, according to the theory, will be delivered at the kathode, either by direct decomposition or by diffusion; negative ions will, in the same way, appear at the anode. If, as we must assume by analogy from liquids, a certain normal force is required to effect the interchange of electricities at the electrode, this will become covered, in the first instance, with the ions until the necessary normal force is obtained. But we are face to face with the questions previously raised relating to the distribution of ions against the surface of the kathode. If the conditions are such that positive gaseous ions behave partly, at any rate, as a gas; if, instead of clinging to the electrode, they form an atmosphere round it, the fall of potential at the kathode is explained. The law according to which their density diminishes as the distance from the electrode increases depends on an experimental term, as has been stated, and I have not yet arrived at a satisfactory theoretical foundation for the law; but various suppositions may be made, and if we may imagine the layer of positive ions to behave like a thin liquid film having a definite vapour pressure, we may easily imagine that the falling off will take place very much as it actually does. The large fall of potential at the kathode, according to this view, is not so much due to the amount of work which has to be done to effect the interchange of electricity, but chiefly to the fact that for the same surface density at the kathode the thickness of the polarising layer is greater, which must necessarily increase the fall of potential. Thus, if σ is the surface density, and D the molecular distance, the fall of potential would be $4\pi v^2 D \sigma$, if the ions covered the kathode as in an electrolyte; but, according to the observed law, the potential in the neighbourhood of the kathode is given by

$$V = V_0(1 - e^{-\kappa x}),$$

which gives for the surface density

$$\kappa V_0/4\pi v^2, \text{ so that } V_0 = 4\pi v^2 \sigma / \kappa;$$

but $1/\kappa$ is of the order of magnitude of a millimeter, and this shows how much the fall of potential is increased by the increased thickness of the layer. Comparing the two expressions, we may say that the fall of potential at the kathode would be the same as in an electrolyte if in the latter case the mean distance of the polarising layer from the kathode was $1/\kappa$ instead of the molecular distances. The numerical values for $1/\kappa$ are, on the average, about six or seven times as great as the mean free path.

According to this view we may explain why gases in their sensitive state, like flames, behave differently to positive and negative charges. A positive charge will attract the negative ions, which will arrange themselves on the surface, and the requisite difference of potential will at once establish itself. But if a conductor placed in the flame carries a negative charge, the layer within which the positive ions collect will be deeper, and the potential of the conductor may not be sufficient to complete the layer so as to produce the necessary normal force.

It also appears that, just as minute chemical changes affect the polarisation in the electrolyte, so will all similar changes affect in the same proportion the fall of potential at the kathode. If I am right, we must consider the conditions of impact between the metal and the ions, or between the gas and the ions, to be different according as the ions have a positive or negative charge, and this leads us to the next point which it will be necessary to discuss.

If the law of impact is different between the molecules of the gas and the positive and negative ions respectively, it follows that the rate of diffusion of the two sets of ions will in general be different; let us see whether we can find any experimental evidence which may throw light on this point. I think there is some reason to believe that the negative ions diffuse more rapidly, and we may at once trace one of the consequences of such a difference of diffusion. Looking at the positive part of the discharge, which shows no signs of a bodily electrification anywhere, at any rate when there are no stratifications, a quicker negative diffusion means, just as in the case of the so-called migrations in electrolytes, an accumulation of ions at the positive pole. That is to say, at the anode a certain number of the ions must recombine again to form a neutral molecule. It has already been mentioned that at the kathode we must imagine decompositions to be going on, continuing during the discharge, because we know that the necessary electrical forces are maintained there. If the discharge is steady, then decomposed atoms must unite somewhere, and, as just suggested, the reunion may take place at the anode; or it may already take place in or just beyond the negative glow. The two questions are intimately connected. If the molecules are decomposed in one part of the tube and reunite in another, the ions in between cannot travel at the same rate. What leads me to believe in a quicker diffusion of negative ions is the fact described in my former paper, that in the neighbourhood of a discharge, positive bodies apparently become neutralised more quickly than negative ones. I think there runs throughout the whole set of experiments a general tendency for the negative ions to be drawn more quickly than positive ions towards the oppositely charged bodies. Some observations on flames also point the same way. Gold-

stein found, in some of his experiments, that when an electric current passing through a gas is forced through a narrow opening many of the phenomena seen near the kathode appear on that side of the opening which faces the positive pole. It is also known that, if a current passes through a funnel-shaped opening, the fall of potential required is greater in one direction than in the other. Finally, if the current is discontinuous, and a point on the outside of a glass tube is connected to earth, certain phenomena are seen which have been specially investigated by Messrs. Spottiswoode and Moulton. All these facts I believe to be capable of explanation if we remember that, whenever a current passes between solids of different conductivities, a certain surface electrification is necessary to satisfy the conditions of continuity. Gases do not follow Ohm's law, and there will in all probability be an electrification whenever the cross-section alters. The different behaviour of positive and negative electrification will come into play, and this, together with the different rate of diffusion of different ions, will, I believe, be found sufficient to explain the phenomena.

The effect of ultra-violet light on a negatively electrified body is probably due, as has been pointed out, to a chemical action, but we have further to assume that this action is not set up on a positively charged body. If this view is correct, we shall have to take the law of impacts between the gas and the metal to be modified in such a way that a chemical effect only takes place when the metal is charged negatively.

Stratifications.

It is generally considered that the most important test of any theory of the discharge is to be found in the way in which it can explain stratification. Very little is known about the circumstances which produce stratifications, and they show by their lawless behaviour that they are rather to be considered as irregularities in the discharge than as matters of primary importance.

According to our view, the regular diffusion of ions in the positive part of the discharge can only be maintained by a balance of very delicately-adjusted phenomena. The two kinds of ions diffuse with different velocities; they will tend to recombine together, and will occasionally do so. If so, and if the current does not cease to be steady, we must have as many fresh dissociations as combinations in each part of the tube. It does not seem impossible that there may be several stable ways in which the current may pass. It is possible that, besides the discharge which passes as I have just explained, there may be another in which the tube is divided into a succession of parts in which the decompositions alternately outnumber the

recombinations and *vice versâ*. Such a tube would show phenomena very similar to stratifications. This is only a suggestion to show that the theory may ultimately be found sufficient to cope with this difficulty. At present it seems to me to be an open question whether the stratifications are ever seen in perfectly pure gases.

The Dark Space.

No satisfactory explanation has yet been given of the division of the appearance round the kathode into three parts: the first luminous layer, the dark space, and the glow. The division between the dark space and the glow is often very sharp, and it is necessary to discuss how the rapid change in luminosity can be accounted for. It has been suggested that the extent of the dark space represents the mean free path of the molecules. If particles are projected from the kathode at low pressures, comparatively few will impinge in its immediate neighbourhood, but with increasing distance the number of impacts will increase. It has been pointed out by others that the extent of the dark space is really considerably greater than the mean free path of the molecule, calculated according to the ordinary way. My measurements make it nearly twenty times as great. This, however, is not in itself a fatal objection, for, as we have seen, the mean free path of an ion may be different from that of a molecule moving among others. I cannot, however, reconcile the sharpness of the inner boundary of the glow with the explanation given. If the luminosity only depended on the number of impacts, we should expect the parts adjacent to the electrode to be dark and gradually to increase in intensity outwards. The positive ions approaching the kathode would still further reduce the difference in luminosity. I have endeavoured to ascertain the experimental conditions which determine the shape of the boundary of the dark space. The first supposition tested was, whether the boundary was always an equipotential surface. If so, the velocity of the particle projected from the negative electrode would be the same all over the boundary, and we might imagine that the luminous appearance of the glow depends on some minimum kinetic energy which the impinging particles must possess. The darkness is, however, not limited by an equipotential surface.

A large cylindrical vessel contained two negative electrodes parallel to the axis of the vessel. The anode was formed by a cylindrical wire netting surrounding the kathodes. Under these circumstances the dark space and glow present some peculiarities, which I shall describe on another occasion. The shadow phenomena described by Goldstein are beautifully seen, and can be photographed, and as the sides of the glass vessel do not interfere (as it now appears they did

in Goldstein's original experiments), I have been able to supplement his observations in several details. At present I only wish to state that the edge of the dark space is, under these circumstances, far from being an equipotential surface; so we must look for some other explanation. We can assure ourselves in another way that it is not a certain minimum kinetic energy which determines the boundary of the dark space. In my previous Bakerian Lecture I followed others in the statement that an increase of current diminishes the thickness of the dark space; but this I find is not correct. If the dark space is carefully watched while the current is diminished or increased by altering the resistance of the circuit, it is seen to contract or expand slightly, always being widest when the current is strongest. Such an increase of current is accompanied by an increased fall of potential; the difference of the potential at which the dark space ends can therefore be altered at will.

I can at present only think of one way of accounting for the facts, but wish for the present to express my views on this point with due caution.

From the magnetic experiments it appears that the velocities of the molecules are reduced quickly in the luminous glow, but not at any rate to the same extent in the dark space. If that is the case, there must be some change in the law of impacts, as we pass from the dark space into the glow; and the simplest supposition to make seems to me to be that the strength of the electric field is an important factor in the transformation of energy which takes place in the collisions. We may imagine that if the electric field is sufficiently strong, the ion will not lose much of its energy during impact, but that in a weak field the velocities are reduced at a much quicker rate. It is clear that if the molecular forces are strong, two molecules must approach much more closely together before their mutual action comes into play, and therefore what must be considered an impact must happen more seldom in a strong than in a weak field. Near the edge of the dark space the electric forces are found to diminish very rapidly, and it is a question worth investigating whether the edge of the dark space is a surface at which the electric force has some constant critical value. I know of no facts which are against this view, and my experiments have hitherto all been consistent with it. The slight widening of the dark space by increase of current would at once be explained if my hypothesis is correct. In the above-mentioned case of two parallel kathodes, there is always a luminous layer in the equidistant plane between them, even when the width of the dark space due to one kathode alone extends sufficiently far to include the other. In this plane the fall of potential is easily seen to be small, and the shape which the dark space assumes seems to me to agree very well with the supposition that there is a critical rate of

potential which determines the edge of glow. But this point must be left to be settled by future experiments.

As regards the inner luminous layer closely adjacent to the negative electrode, it seems due to the positive ions approaching the kathode, and not, like the glow, to the negative ions projected away from it. This is shown by the fact that a wire placed inside this layer casts a shadow *towards* the kathode, and also by the distortion it experiences in a magnetic field. It is remarkable that this luminosity, due to the impact of positive ions, shows according to Goldstein, at any rate in the case of nitrogen, the spectrum of the positive part of the discharge.

Conclusion.

We may now in conclusion shortly summarise the results arrived at. A gas in its normal state contains no free ions, but, if through any chemical or physical causes the molecules are broken up in an electric field, ions form, and the gas becomes a conductor. Supposing the difference of potential of two electrodes is gradually increased, a point will be reached at which a spark will pass, that is to say, the molecules will be broken up by electric forces, the positive ions diffusing towards the kathode will tend to form a polarising layer of finite thickness, increasing in width as the pressure diminishes. If the discharge becomes steady, the decompositions are continuously kept up at the kathode, the negative ions being projected with great velocity away from it. These ions will move through the so-called dark space without much loss of energy by impacts, but when, probably owing to sufficient diminution in the electric force, the impacts become more frequent, the translational energy becomes transformed into the luminous vibrations of the glow. The positive ions forming an atmosphere round the kathode must have a greater velocity the nearer the kathode, where their energy becomes visible in the first luminous layer. Whether decompositions take place only at the electrode or through a finite distance from it is at present an open question, nor can we decide as yet whether the negative molecules projected outwards are the main carriers of the current inside the dark space. In the dark space the negative ions will accumulate and meet the positive ions proceeding from the positive part of the discharge. We shall expect at some point towards the outside of the glow the free ions to become more numerous than in other parts of the discharge. Here we find a small fall of potential and no luminosity; this is the dark interval separating the positive part of the discharge from the negative glow. A number of ions probably reunite in this part to form molecules, and in case it should ultimately be found that positive and negative ions diffuse with the same velocity, we should have to conclude that as many molecules as are

decomposed at the kathode recombine in this dark interval. If, as seems more probable to me, it should be found that the negative ions diffuse more rapidly, the recombination will in part take place at the anode. If the conditions in the tube are such that the gas may divide into layers, such that in alternate strata the decompositions outnumber the recombinations, and *vice versâ*, stratifications will form.

Such is the general outline of the theory, which may have to be modified in detail, but which, I believe, has a strong element of truth in it.

The possibility of a volume electrification is denied by some of Maxwell's disciples, who look on a current of electricity as on a flow of an incompressible liquid in a closed circuit. But there is nothing, as far as I can see, in the conclusions I have drawn from the gas discharges which is inconsistent with the fundamental tenets of Maxwell's theory, however much they may disagree with the accessory embellishments with which that theory is occasionally adorned. There may be a volume electrification without interfering with the equation of continuity of an incompressible liquid as long as we admit the possibility of displacement currents and displacements in conductors, and I see nothing improbable in this. The ordinary equations for the currents in a non-homogeneous solid (or any solid if inequalities of temperature are taken into account) give a volume electrification which can only be destroyed by the introduction of a quantity which is analogous to hydrostatic pressure, and the sole purpose of which is to destroy all electrifications except at the surface of bodies. We know of no physical phenomena which can justify the introduction of such a quantity, which seems to me unnecessary. The existence of a volume electrification can be shown to exist when a current passes from one liquid to another floating on its surface. Chemical effects are observed in the region in which the liquids begin to mix, and these can be explained by the electrification which accompanies each change in electric conductivity. Maxwell's equations assume conductors to be homogeneous throughout; whenever we are dealing with average effects only, this assumption is justified. We deduce, in a similar way, the equations which represent the transmission of light by assuming that each transparent body is replaced by a homogeneous medium having certain properties. But although this simplification is allowable in discussing some of the phenomena, there are others in which it becomes necessary to go a step further, and, considering the structural constitution of the body, to take into account separately the effects of the medium separating the atoms, and the effects of the atoms themselves. In all branches of physics we are gradually forced by the advance of knowledge to abandon the assumption of homogeneousness, and if that is done, no further difficulty stands in the way of bodily electrifications; for

we may take them to be really only surface electrifications between the atoms and the medium.

I have offended in another manner against so-called modern views of electricity, for I have spoken of positive and negative electricity as real substances possessing a separate existence. I have tried to place myself, however, under the shelter of recognised authority by quoting at the top of this lecture Helmholtz's saying that we have as much ground for the supposition that electricity has an atomic constitution as we have for the atomic constitution of matter. We must trust to the future to bring this view into harmony with the electromagnetic theory of light, which may be accepted now as an established fact. There is no real antagonism between the two views. If ever we are able to explain chemical and gravitational attraction by the stresses in a medium, we shall still find it convenient to speak of atoms and molecules; and in the same way the belief in an electric strain and stress is consistent with a belief in something in the atom from which the strain proceeds, and which may be taken as the elementary quantity of electricity. Even taking the extreme view that electric stress is due to vortex filaments in the ether, we need only assume all these filaments to have the same intensity, and some to end at the surface of atoms, in order to reconcile apparently antagonistic views. But there is no need to commit ourselves at present to any particular ideas. In some electric phenomena we shall find it most convenient to speak of electric strain and stress (displacement I think to be a misleading term, which, however, has come too much into use to be dispensed with); in other, and at present more numerous, cases, we shall still continue the old nomenclature, and speak of positive and negative electricity as real quantities. The subject of electro-chemistry is one of primary importance in the present state of science. The different behaviour of positively and negatively electrified particles points, as I have tried to explain, to an unsymmetrical modification of molecular forces by electrification. It is not sufficient to add geometrically the effects of molecular and electrical action, but it is necessary to take account of the interference between chemical and electrical forces. The exact nature of this interference must partly be solved by chemical investigation, but the discharges of electricity through gases still promise a rich harvest to the investigator.

Appendix.

“The Discharge of Electricity from Glowing Metals.” By
ARTHUR STANTON, B.A.

It has long been known that certain bodies undergoing chemical decomposition are capable of discharging electricity through the

surrounding air. A few desultory experiments were made in Dr. Schuster's laboratory, during the hot days of summer about two years ago, as to this discharge when the body was decomposed in the focus of a large concave mirror. The method, depending on exceptionally brilliant weather, is necessarily inconvenient in this country. Subsequently, during the Long Vacation, I made experiments in the same direction, and tried to use a piece of hot metal for the supply of heat to effect dissociation. These attempts led to an observation of the conditions under which a hot electrified piece of copper or iron could retard a charge of electricity at a good red heat. I observed in my first experiments that if a copper soldering bolt, heated to full redness by a gas blowpipe, was placed on an insulating stand and negatively electrified, discharge took place very rapidly, and occurred so long as the bolt remained visibly red; that if the bolt was repeatedly heated in an oxidising flame, and electrified, discharge became continuously slower, and that ultimately the copper was capable of retaining a charge perfectly at a full red heat. If the copper bolt, being in the state last described, was allowed to cool completely, the oxide of copper chipped off, and the metal, on heating to redness, behaved generally as at the commencement of the experiments.

An iron bar was found to behave similarly.

The experiment was afterwards repeated, with the substitution of a wire kept hot by a current for the massive bar of metal.

In the later form of the experiment, the hot body was connected to earth, and the discharge of an electrified conductor in the neighbourhood observed. The wire was wound upon a mica frame with thick copper terminals, which served to give the frame rigidity; the other electrode of the system consisted of a clean flat copper plate, at a distance of 2 or 3 cm. from the frame. The wire used varied from 0.3 to 0.5 mm. in diameter, the length being about 60 cm. Both the frame and the flat plate contiguous to it were enclosed in a glass or cylinder surrounded by water to keep it cool, and provided with tubes for the introduction of gases.

The following are the results obtained:—

First, if the conductor contiguous to the wire be positively electrified.

Here the clean copper wire on becoming red-hot rapidly discharges the conductor; when a uniform film of oxide is formed, the discharge ceases.

If the containing vessel be now filled with hydrogen, and the wire again heated, a similar discharge takes place until the oxide film is completely reduced; the conductor thereafter retains its charge perfectly.

Secondly, if the conductor be negatively electrified.

In this case, the copper wire must be heated for a longer time in air before it ceases to effect the discharge, and there is not the same sharpness of definition between the two states. The phenomena observed on heating the now oxidised wire in hydrogen differ also in this case; the hot wire not only effects discharge during the reduction of its oxide coat, but continues to possess this power certainly for a long time to the same degree. Hence, a red-hot copper wire in hydrogen exhibits the curious property of retaining perfectly a charge of negative electricity, and discharging instantly a positive electrification. The hydrogen used was fairly dry, and free from any sensible taste or smell.

In dry nitrogen, the results were similar to those obtained with hydrogen. The gas was carefully dried, and passed for eight or nine hours over the copper before the electrical tests were made; the red-hot copper wire retained a negative charge, but not a positive one.

The above experiments were all made in Dr. Schuster's laboratory, and, in fact, under his immediate supervision. Dr. Schuster has suggested that they are of sufficient interest to publish in their present state, because they show more clearly than the experiments with platinum the nature of the chemical action. In the case of platinum, there is, of course, the advantage that the metal remains generally in the same state, but it is much lessened by the very marked and complex effects of surface condensation and occlusion.

The potential of the bodies used was observed by means of an ordinary gold leaf electroscope, and was such as to cause a large divergence of the leaves. In all cases where discharge took place, it was found easy to cause complete collapse of the leaves.

It is proposed to supplement this paper with one dealing with the phenomena in pure and perfectly dry gas.